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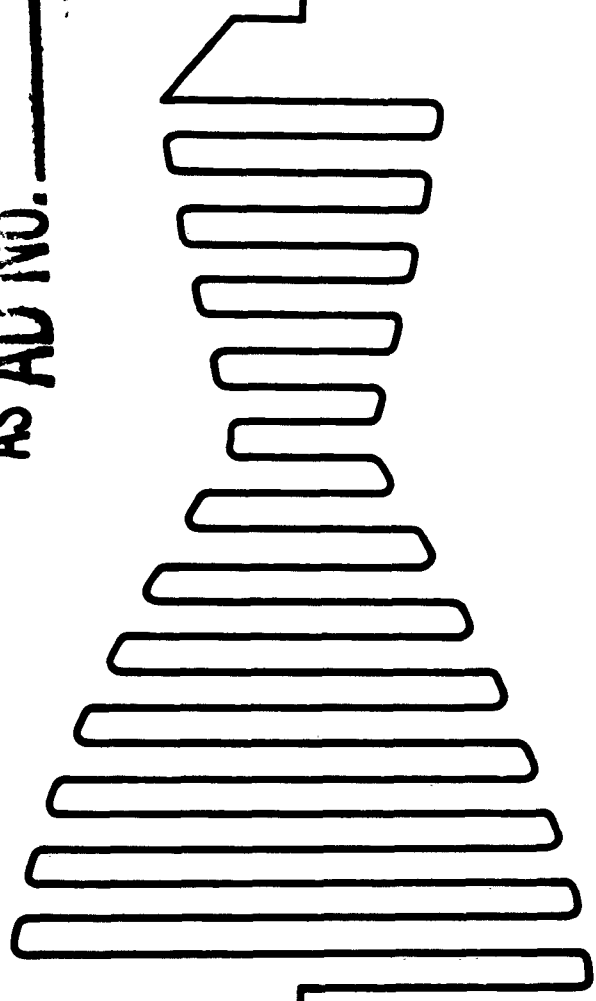
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ROCKETDYNE
A DIVISION OF NORTH AMERICAN AVIATION, INC.
CANOGA PARK, CALIFORNIA

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RESEARCH IN HYBRID COMBUSTION,
QUARTERLY REPORT FOR PERIOD
ENDING 31 AUGUST 1962

ROCKETDYNE

A DIVISION OF NORTH AMERICAN AVIATION, INC.

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FOREWORD

This quarterly progress report covers the research accomplished under contract Nonr -3016(00) through 31 August 1962. The personnel associated with this program were M. V. Peck, T. Houser and H. N. Chu. Dr. S. S. Penner was a consultant.

ABSTRACT

The radius vs time data taken at two oxygen flowrates were fitted by the empirical equation $r = A + Bt^C$. The instantaneous burning rate, \dot{r} , is obtained by differentiation of this equation. The thermocouple measurements were described by the psuedo-steady-state heat conduction equation $T = T_s \exp(-bx/k)$. A theoretical development from the von Karman fundamental equations for aerothermochemistry did not improve the theoretical model previously developed.

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INTRODUCTION

This research program in hybrid combustion has been concerned with the investigation of the processes involved in the reactions between solid fuels and gaseous oxidizers. The purpose of these studies, in the presence of a flame, has been to develop a suitable model for the hybrid combustion processes.

In previous reports (Ref. 1 thru 5) the experimental results indicated that the hybrid combustion of plexiglass and gaseous oxygen was consistent with the idea that the combustion rate is largely controlled by diffusion processes. A simplified theory of hybrid combustion of the same order of sophistication as the classical treatment of Burke and Schumann (Ref. 6) for the flame shape in cylindrical diffusion flames was presented for the plexiglass-oxygen system (Ref. 1). With proper definition of the diffusion parameters, this theory may be applied to all types of flow and, in particular, to the turbulent flow conditions examined experimentally.

The purpose of the more recent work has been to define better the contributions of the experimental parameters to the observed regression rates (Ref. 4 and 5). In this report period effort was directed toward obtaining better defined functions of radius with time at the two entrance Reynolds numbers (55,000 and 36,000) and from these functions calculating instantaneous regression rates. In addition the problem of temperature profile in the solid fuel was explored further.

EXPERIMENTAL APPARATUS AND PROCEDURE

The basic apparatus (Fig. 1) has been described in previous reports (Ref. 1 and 5). The tubular configuration is used for the present experimental program. The mixing and flow stabilization tube, which was a 2-sq in. duct, has been replaced by a 1-inch-diameter tube to prevent the turbulence caused by the abrupt change in diameter at the entrance. In a typical run, a fuel cylinder composed of 3 by 3 by 2-inch blocks with 1-inch diameter concentric holes aligned with the holes of the facing and backing plates, is burned for the specified time. The axial length, the composition and temperature of fuel, the time of burning, and the initial diameter of the concentric hole may be varied. Thermocouples may be imbedded between adjacent fuel blocks at any desired radial distance to measure the increase in temperature at that position as the burning surface approaches.

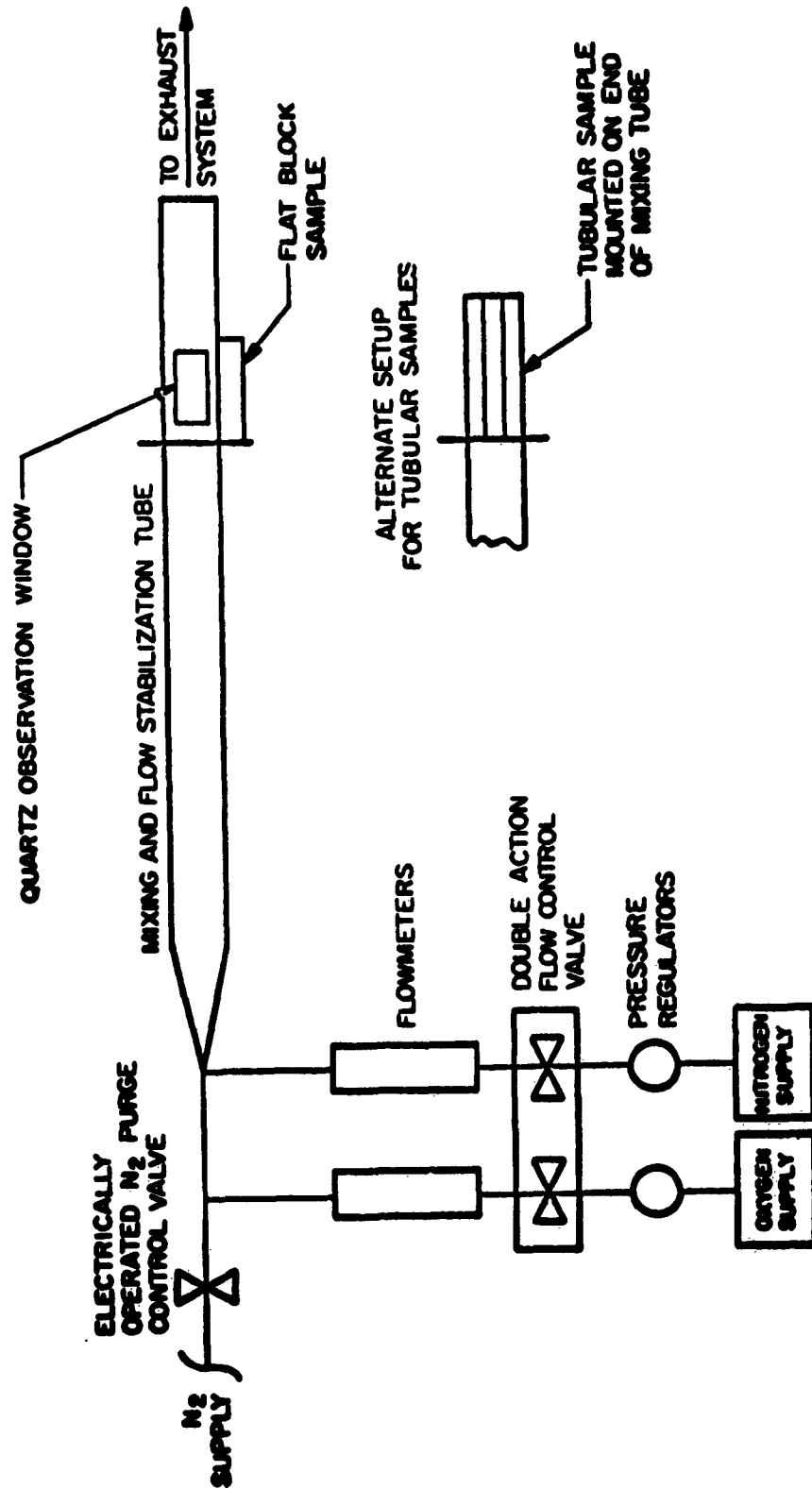


Figure 1. Hybrid Combustion Apparatus

EXPERIMENTAL RESULTS AND DISCUSSION

DEPENDENCE OF RADIUS ON TIME

To determine the change in the radius of the fuel surface with burning time, runs have been made at various burning times with plexiglass (PMMA) fuel blocks and oxygen at two entrance Reynolds numbers of approximately 55,000 and 36,000. The final radius was calculated from the weight burned for each axial position at each burning time, assuming symmetrical burning.

Since a line pressure of about 3 or 4 psig was observed at the start of combustion when $Re_{2r_0} = 55,000$ (which reduced to 0 psig at 10 to 15 seconds), a second series of runs was made at the lower flowrate ($Re_{2r_0} = 36,000$) where no initial line pressure was observed. Twelve runs were made at this oxygen flowrate using an axial length of 24 inches.

Figure 2 is a comparison of the two flowrates, in which a typical plot of the final radius vs burning time for block 3 (axial position of 5 inches) for both $Re_{2r_0} = 55,000$ and 36,000 is shown.

It was hoped that it would be possible to secure a definition of the radius (r) as a simple function of time (t) which could be utilized over the entire range of time. The Research Multiple correlation computer program which applies various statistical tests in attempting to obtain the best fit of the supplied functions to the experimental data, was used to acquire the best function.

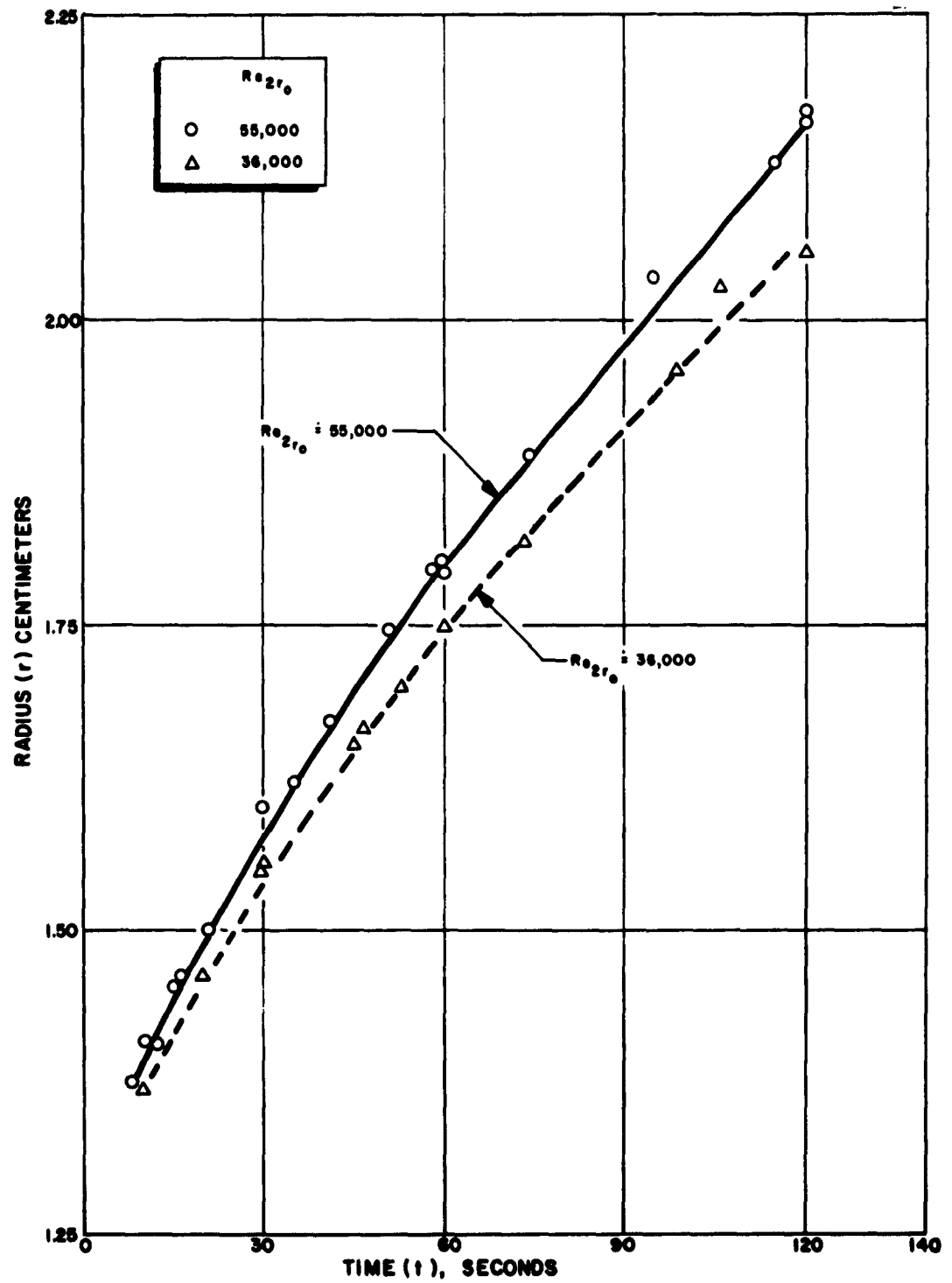


Figure 2. Radius of PMMA Block 3 vs Burning Time

Among the functions fitted to the r vs t data was $r = A + Bt^c$, where $c = 0.75$ for $t \leq 60$ and $c = 1.0$ for $t \geq 60$ gave the best fit. The fit for a single function over the entire time range was almost always poor at the low times. The curve fitting constants are summarized in Tables 1 and 2; the curves for block 3 are shown in Fig 2. Upon differentiation of $r = A + Bt^{0.75}$, \dot{r} was equal to $0.75 Bt^{-0.25}$, which is infinite at time zero. Although this is unrealistic from a physical standpoint, it can be compared to the infinite heat flux for a semi-infinite slab at time zero (i.e., time zero is not physically defined in either case). Therefore, the equation for r does not have to be defined at $t = 0$ to make the r function useful. Other functions were not as good, as shown below.

The r vs t data was also fitted well by the function $t = A + Br + Cr^2$ which yielded a rate equation $\dot{r} = (B + 2Cr)^{-1}$. This equation is finite at time zero. However, since experimentally the burning times are defined and then the radii determined, it is statistically improper to reverse this and define t as the dependent variable and r as the independent variable.

The function $r = A + Bt + Ct^2 + Dt^3$ appeared to be a satisfactory fit for the r vs t data. In general, A , B and D were found to be positive and C was negative. At high t the calculated rates (\dot{r}) were found to increase because the positive term $3Dt^2$ increases much more rapidly than the negative term $2Ct$. This is impossible since no inflection was observed in the r vs t plots, thus the fit was not as good as first believed.

TABLE 1

CURVE FITTING CONSTANTS*

	A		B x 100	
	Re _{2r₀} = 36,000	55,000	36,000	55,000
Block				
1	1.27	1.32	2.67	2.35
2	1.23	1.25	2.54	2.68
3	1.24	1.25	2.36	2.50
4	1.24	1.28	2.39	2.46
5	1.24	1.27	2.49	2.62
6	1.22	1.26	2.60	2.79
7	1.23	1.26	2.52	2.87
8	1.23	1.28	2.49	2.83
9	1.24	1.28	2.42	2.92
10	1.25	1.30	2.46	2.88
11	1.26	1.32	2.58	3.15
12	1.26	1.30	2.99	2.53

* $r = A + Bt^{0.75}$ for $t \leq 60$

TABLE 2

CURVE FITTING CONSTANTS*

	A		B x 1000	
	Re _{2r₀} = 36,000	55,000	36,000	55,000
Block				
1	1.60	1.61	3.9	3.5
2	1.47	1.50	5.3	5.6
3	1.44	1.44	5.3	6.0
4	1.45	1.47	5.1	5.5
5	1.49	1.51	4.8	5.4
6	1.50	1.54	5.0	5.3
7	1.43	1.54	5.7	5.5
8	1.42	1.54	5.9	5.8
9	1.38	1.55	6.1	6.0
10	1.42	1.55	6.2	6.4
11	1.43	1.60	6.4	6.4
12	1.48	1.68	7.6	6.6

*r = A + Bt for t ≥ 60

It should be noted that the linear portions of the curves for t above 60 seconds are the best straight lines through the data and are continuations of the curves below 60 seconds.

INSTANTANEOUS BURNING RATES

The instantaneous burning rates can be tabulated in two ways: \dot{r} vs z at constant time and \dot{r} vs z at constant r . It is believed that the values for blocks 1 and 12 exhibit end effects and so have not been included in the tabulations.

Burning Rate as a Function of Time

By differentiation of the empirical equations of r vs t , it is possible to obtain the instantaneous rates for any time and axial positions. Representative values are summarized in Tables 3 and 4. The \dot{r} changes by a factor of about 4 at both flowrates over the burning times used. At the lower flowrate, the \dot{r} does not appear to change significantly with z , whereas the higher flowrate gives a steadily increasing \dot{r} at all times.

TABLE 3
INSTANTANEOUS RATES
(cm/sec x 10³)
 $Re_{2r_0} \div 36,000$

Block	2	3	4	5	6	7	8	9	10	11
Time, sec										
1	19.1	17.7	18.0	18.7	19.5	18.9	18.7	18.2	18.5	19.3
5	12.7	11.9	12.0	12.5	13.1	12.6	12.5	12.1	12.4	12.9
10	10.7	10.0	10.1	10.5	11.0	10.6	10.5	10.2	10.4	10.9
20	9.0	8.4	8.5	8.8	9.2	8.9	8.8	8.6	8.8	9.1
30	8.1	7.6	7.7	8.0	8.3	8.1	8.0	7.8	7.9	8.3
40	7.6	7.1	7.1	7.4	7.8	7.5	7.4	7.2	7.4	7.7
50	7.2	6.7	6.8	7.0	7.3	7.1	7.0	6.8	7.0	7.3
60	6.8	6.4	6.4	6.7	7.0	6.8	6.7	6.5	6.7	6.9
>60	5.3	5.3	5.1	4.8	5.0	5.7	5.9	6.1	6.2	6.4

TABLE 4

INSTANTANEOUS RATES
(cm/sec x 10³)

Re_{2r₀} ÷ 55,000

Block	2	3	4	5	6	7	8	9	10	11
Time, sec										
1	20.1	18.7	18.4	19.6	21.0	21.6	21.2	21.9	22.3	23.6
5	13.4	12.5	12.3	13.1	14.0	14.4	14.2	14.7	14.9	15.8
10	11.3	10.5	10.4	11.0	11.8	12.1	11.9	12.3	12.6	13.3
20	9.5	8.9	8.7	9.3	9.9	10.2	10.0	10.4	10.6	11.2
30	8.6	8.0	7.9	8.4	9.0	9.2	9.1	9.4	9.5	10.1
40	8.0	7.5	7.3	7.8	8.3	8.6	8.4	8.7	8.9	9.4
50	7.6	7.1	6.9	7.4	7.9	8.1	8.0	8.2	8.4	8.9
60	7.2	6.7	6.6	7.1	7.5	7.7	7.6	7.9	8.0	8.5
>60	5.6	6.0	5.5	5.4	5.3	5.5	5.8	6.0	6.4	6.4

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Burning Rate as a Function of Radius

At the higher flowrate the radius varies with axial position, and therefore, at any specified time, the rates are not strictly comparable because the Reynolds number varies with radius. It is believed that a better basis of comparison of \dot{r} vs z would be at equal radii rather than at equal burning times. Table 5 summarizes the rates at three radii for $Re_{2r} = 36,000$ and $55,000$. The ratio of the rates at the two oxygen flowrates (as given in Table 5) are summarized in Table 6, and the dependence on axial length is observed for the ratio.

At this point the effects of turbulence on regression rates must be considered as indicated by these two sets of data. From the relative regression rates at the two oxygen flowrates, and assuming H_2O and CO or CO_2 as the products of oxidation, the relative volume rates of flow can be calculated. It is found that the relative volume rate of flow changes very slightly with z and, in fact, appears to get smaller; that is, at the entrance the ratio of oxygen flowrates is about 1.50, and at block 11, the flowrate ratio of oxygen and products is about 1.42 for H_2O and CO , and 1.46 for H_2O and CO_2 . Although the absolute volume rate of flow increases with z , the relative flowrate does not. Since these flowrates are at constant radius, the relative turbulence must remain about constant. The relative regression rates remain constant at about 1.10 up to 10 inches, and then steadily increase to above 1.35, at 20 inches.

TABLE 5

INSTANTANEOUS BURNING RATES, $\dot{r} \times 1000$ cm/sec
Constant Radii

Radius, centimeters 1.50			1.65		1.80	
Block No.	$Re_{2r_0} = 36,000$	55,000	36,000	55,000	36,000	55,000
2	8.7	9.5	7.5	8.2	6.8	7.3
3	8.0	8.8	6.8	7.5	6.2	6.7
4	8.1	8.9	7.0	7.5	6.3	6.7
5	8.5	9.5	7.3	8.1	6.6	7.2
6	8.8	10.2	7.7	8.7	6.9	7.8
7	8.6	10.6	7.4	9.0	6.7	8.1
8	8.4	10.7	7.3	9.0	6.6	8.0
9	8.2	11.2	7.1	9.4	6.4	8.4
10	8.5	11.8	7.3	9.8	6.5	8.7
11	9.2	13.2	7.8	10.8	7.0	9.5

TABLE 6

RATIO OF REGRESSION RATES AT THE TWO FLOWRATES
($Re_{2r_0} = 55,000$ and $36,000$)

Radius, centimeter	1.50	1.65	1.80
Block			
2	1.09	1.09	1.07
3	1.10	1.10	1.08
4	1.10	1.07	1.06
5	1.12	1.11	1.09
6	1.16	1.13	1.13
7	1.23	1.21	1.21
8	1.27	1.23	1.21
9	1.37	1.32	1.31
10	1.39	1.34	1.34
11	1.43	1.39	1.36

It appears that the major difference between the two flows is that the concentration of oxygen remains higher down the burner. This indicates two possible explanations for the observed change in relative rates:

1. The average gas temperature may remain higher at the higher flow since the combustion can be more complete, and/or
2. Oxygen may reach the surface and aid in the unzipping of the polymer; thus, as the concentration difference becomes greater down the burner, the regression rate differences may also increase.

These two possibilities cannot be differentiated at this time and both may be operating.

THERMOCOUPLE MEASUREMENTS

The results of the thermocouple measurements are summarized in Table 7 . The experimental data was found to be fitted by the following equation:

$$T = T_s \exp (-bx/k)$$

$$k = \text{diffusivity in solid, cm}^2/\text{sec}$$

$$x = \text{linear distance from thermocouple to burning surface, centimeters}$$

$$(x + r) = \text{the sum of radius and distance to the surface, a constant}$$

$$T = \text{temperature at thermocouple referenced to block temperature}$$

$$T_s = \text{surface temperature referenced to block temperature}$$

$$r = \text{average burning rate, cm/sec}$$

$$b = \left[k/(x + r) + \dot{r} \right]$$

TABLE 7
THERMOCOUPLE RESULTS

Run No.	T_s^*, C	Rates $\times 10^3$ (cm/sec)**		Ratio Calculated/Observed	Run Time, seconds
	$Re_{2r_0} =$	Observed	Calculated		
1431	115	9.1	13.9	1.53	59
1432	205	9.7	14.2	1.47	41
1433	110	9.5	13.2	1.39	51
1434	120	8.2	8.0	0.98	95
1435	90	8.6	9.8	1.14	74
1437	95	10.1	13.6	1.35	35
1441	160	7.5	7.9	1.05	115
	$Re_{2r_0} =$				
1444	170	8.4	12.8	1.53	53
1446	110	8.6	11.1	1.29	45
1447	105	7.8	10.1	1.29	73
1448***	115	8.8	13.2	1.50	47
1449***	125	7.5	9.2	1.23	99
1450	105	9.3	13.0	1.40	30
1451	175	7.3	8.0	1.10	106

*Referenced to block temperature of approximately 25 C
 **Calculated rates are derived from the slope of T vs x curves, the observed rates are the averages for the run.
 ***The axial distances of the thermocouple for these two runs were 18 inches, for all others it was 4 inches.

This equation was obtained using the assumptions that temperatures and rates were independent of time (steady state and constant regression rates) and solving the moving boundary differential equation for a cylindrical surface (Ref. 5, Eq. 7):

$$\delta T / \delta t = k \delta^2 T / \delta x^2 + \left[k / (x + r) + \dot{r} \right] \delta T / \delta x = 0$$

or

$$d^2 T / dx^2 = -(b/k) dT / dx$$

Figure 3 shows typical examples of the consistency of fitting this equation to runs 1431 (59 seconds burning time) and 1432 (41 seconds burning time). As indicated in Table 7, the calculated and observed burning rates are in fair agreement. This, coupled with the good fit of the derived equation to the temperature-distance data, indicates that the incorrect assumptions of steady state and constant burning rate necessary for the derivation of the equation do not prohibit its use.

A discussion of the probable error and the significance of these measurements is in order. The range of surface temperatures obtained can be explained easily by the uncertainty in the measurement of x , which is known no better than ± 0.3 millimeter. This is indicated by the two curves in Fig. 3. Since this type of error is due to random uncertainty an average over the 14 runs listed in the table should produce an accurate surface temperature, assuming that a systematic error does not influence the data. It is believed that the observed temperature may be somewhat low due to heat losses down the thermocouple wire. This possibility will be investigated experimentally and corrections applied if necessary.

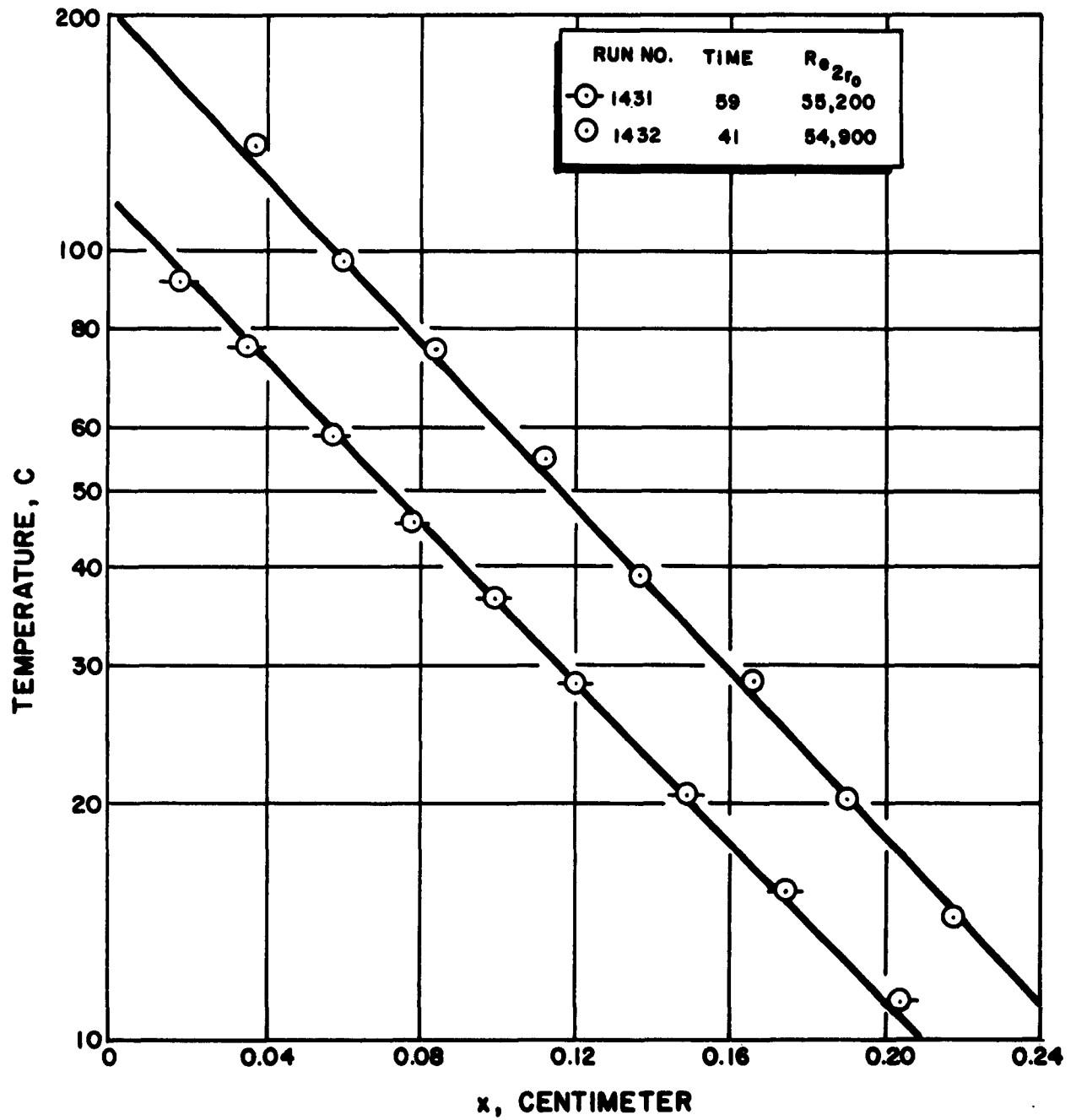


Figure 3. Typical Thermocouple Data

Two conclusions can be drawn from these results:

1. The uncertainty in the x measurement prevents the differentiation of small changes in surface temperatures as would be predicted with time, axial distance, or oxygen flowrate. Thus, much of the discussion on this point in the previous report becomes academic.
2. All of the extrapolated surface temperatures are extremely low, unless the average is raised well over 200 C by a heat loss correction which appears unlikely.

The isothermal degradation kinetics for PMMA indicate that the observed regression rates could not be obtained at these temperatures. This may be an indication that oxygen or other chain-initiating species are reaching the surface and causing weight losses far in excess of those predicted by pyrolysis rate data. This area will be given further consideration.

**FURTHER THEORETICAL ANALYSIS OF DIFFUSION
MODEL PROPOSED PREVIOUSLY**

The experimental study of hybrid combustion processes has concentrated on the burning of solid fuel with gaseous oxidizer and, specifically, the burning of plexiglass with gaseous oxygen. The experimental results have supported the idea that the process by which the fuel and oxidizer are brought together is characterized by diffusion. A simplified theory was developed following the Burke-Schumann approach (Ref. 6) for the laminar diffusion flame. With the high linear flow of oxygen in the restricted cylindrical passage, turbulence must dominate the pipe flow; and therefore, it was necessary that the parameters of the theory be defined for turbulent diffusion. Thus, no distinction is made between turbulent and laminar flow conditions except by appropriately chosen parameters.

Turbulence and diffusion are not the only rate controlling factors. The rate of combustion is limited by the availability of fuel through the rate of gasification. Turbulent flow, heat transfer, species diffusion and chemical energy release all play complicated roles in hybrid combustion. In an effort to evaluate these effects and, possibly, to obtain a simple theory, easy to understand and yet generally applicable, it seemed necessary to review the previous analytical work, then systematically derive and reduce the differential equations involved, in the hope of obtaining a more sophisticated and more appropriate model than the one proposed which was obtained through the Burke-Schumann approach.

The first model was obtained previously with the following assumptions:

1. Chemical reactions are confined to the flame front, considered an infinitely thin mathematical surface close to the wall to which the fuel and oxidizer are delivered in stoichiometric proportions and are, therefore, consumed instantaneously. For this reason no fuel exists in the core and no oxygen exists in the annular region between the flame front and the wall.
2. The pressure gradient is negligible and the linear flow velocities are constant. Hence, the axial velocity term is neglected, and only radial transport by diffusion is considered. This has been assumed to be, primarily, concentration diffusion.
3. Gas mixtures are considered to be binary mixtures composed of the major constituent (either fuel or oxidizer, depending on location beneath or above flame front) and the rest of the gas mixture as an average.
4. The product of gas density and binary diffusion coefficient is assumed independent of radial and axial distances and temperature.
5. No distinction is made between types of flow, and appropriate applicable transport coefficients are to be utilized for the axisymmetric conditions.
6. The binary diffusion coefficients of fuel and oxygen through nonreacting gas are numerically equal.

Applying these assumptions, the continuity equation for the species can be simplified and combined with the boundary conditions to provide a solvable boundary-value problem, and hence, a simplified theory of hybrid combustion as summarized in Ref. 1.

The fundamental equations in aerothermochemistry as proposed by von Karman (Ref. 7) can be the foundation for a more sophisticated theoretical development. It was necessary to simplify these most general equations through proper consideration of the conditions of this specific problem.

The following assumptions and processes (basically the same as those in the first model) were then applied chronologically to obtain a solution:

1. The compressible gas is considered to be in thermodynamic equilibrium, i.e., the concentration of each species is a unique function of the local pressure and temperature
2. Multicomponent gas mixtures are represented by the fictitious binary system of the major component and the other components by average characteristics. The specie continuity equation is completely described by one equation in terms of the mass fraction of the major constituent alone. This eliminates chemical kinetic considerations
3. All parameters are independent of the aximuthal angle, and axisymmetric conditions exist
4. Pressure gradient is negligible

5. By analogy with the Denison (Ref. 8) boundary layer equations for chemical ablating surfaces, the applicable pipe flow equations in mean quantities can be written
6. The cylinder radius is observed not to be a true time variable but a parameter that takes on definite constant values at each finite burning time
7. Existence of a flame front which is the site of all chemical reaction, i.e., an aerothermochemical discontinuity

Through the use of Eulerian coordinates, and suitable transformations and decoupling procedures the fuel, oxygen, and temperature profiles can be estimated. Approximate solutions for the regression rate \dot{m} can be obtained through a method of iteration in which the zeroth order corresponds to the first approach to the simple theory developed earlier. Subsequent estimates for \dot{m} are of the form

$$c \dot{m}_n = c \dot{m}_{(n-1)} - \left[\frac{a}{\dot{m}_{(n-1)}^2} \frac{d\dot{m}_{(n-1)}}{dz'} \right]$$

z' being the function of the axial length. This should yield a measure of the modifying effect on the burning rate of the product of density and axial velocity (ρu) which was neglected in the Burke-Schumann approach.

Numerical calculations demonstrate that the additive term in the above equation decreases the \dot{m} toward the exit in contrast to the experimental results. It is believed that the inaccuracies in the theoretical model are inherent in the assumption that the reactions between oxygen and fuel occur only at the infinitely thin flame front, and that the reactants are in stoichiometric proportions. Physically this assumption is oversimplified

and in the extreme case, after the oxygen has been substantially depleted, the fuel will simply gasify because of the hot gas near it.

Because of the difficulties in defining the experimental quantities utilized in these equations and in solving the differential equations without employing simplifying assumptions which significantly affect the solutions, no further work is planned in this area.

SUMMARY

The r vs t data taken at two oxygen flowrates $Re_{2r_0} = 36,000$ and $55,000$ were best fitted by the empirical equation $r = A + Bt^c$ where $c = 0.75$ for $t \leq 60$ and $c = 1.0$ for $t \geq 60$. Differentiation of this equation yields an equation from which the instantaneous rates can be calculated. These rates have been tabulated as a function of z at both constant burning time and constant r . The ratios of the regression rates at the two flowrates have a dependence on z which cannot be accounted for by changes in turbulence.

The experimental results of the thermocouple measurements could be fitted by the psuedo-steady-state heat conduction equation, $T = T_g \exp(-bx/k)$; an average \bar{r} has been calculated from b . Two conclusions can be drawn from the results: (1) The uncertainty of the linear measurement, x , prevents differentiation of small changes in surface temperatures as would be predicted with time, axial distance or oxygen flowrate, and (2) all extrapolated temperatures are extremely low to account for the observed regression rates from isothermal pyrolysis rates of PMMA. This may indicate oxygen reaching the surface and initiating polymer degradation. The reliability of the temperature measurements will be investigated further.

In an effort to evaluate and, possibly, to improve the simple theory for hybrid combustion obtained via the Burke-Schuman approach, a theoretical development was made, starting with the von Karman fundamental equations for aerothermochemistry. The resultant equations should have shown the modifying effect of including the ρu term neglected previously. Numerical calculations indicate that the additive term decreases calculated

regression rate toward the exit, which is in contrast to the experimental results. It is believed that the prediction of a decrease in mass regression rates is inherent in the flame front assumption.

FUTURE EFFORT

Temperature measurements within the solid fuel will be made with thermocouples of smaller diameter wire. These will be used to determine the error caused in the temperature measurements by the heat losses down the thermocouple wire and as a result of using a relatively large bead.

Burning rate data at increased pressures will be obtained. To check the effect of radiation absorption of the surface, additional burning rate data will be secured with fuel blocks of 0.25- and 0.50-percent carbon in PMMA.

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